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(54) **Thermally converted starches and the method of preparation thereof**

(57) The present invention provides an efficient acid conversion process by which native and modified starches may be treated to afford products with low viscosity and a higher proportion of lower molecular weight compounds than the corresponding aqueous acid conversion processes. Such converted starches demonstrate unique properties and, accordingly, are useful in a variety of products.

EP 1 281 721 A1

Description

[0001] The present invention relates to a process for converting starches. More particularly, the invention relates to an acid conversion process whereby products having low viscosity and high levels of lower molecular weight compounds can be obtained.

[0002] Starches normally have good thickening properties because of their high molecular weight polymeric components. For applications that typically utilize a high starch (i.e., solids) content, such as adhesives, candies and food coatings, the common practice is to use starches that have been converted. The conversion process results in starch products that contain reduced molecular weight polymers and exhibit reduced viscosity.

[0003] The most common conversion methods used in the starch industry include acid hydrolysis, oxidation, pyro-conversion, and enzyme conversion. Except for enzyme conversion, granular starch is used in the modification processes for ease of recovery. This recovery process generally involves a suspension of the final starch product in water, neutralizing the pH, then filtering out the starch product and washing the product with water. Such a process generally removes salts and charged particles, including the smaller molecular weight side products created during conversion.

[0004] The use of aqueous methods to convert starch which utilize the above described recovery method are well-known and described, for example, in publications such as "Starch: Chemistry and Technology", Second Edition, edited by Roy L. Whistler et al., Chapter X; Starch Derivatives: Production and Uses by M. W. Rutenberg et al., Academic Press, Inc. 1984.

[0005] There is a continuing need for an alternative conversion process that provides starches having lower viscosity and high levels of lower molecular weight compounds not heretofore observed in the art.

[0006] The present invention relates to a process for converting starches. More particularly, the invention relates to an acid conversion process whereby products having low viscosity and high levels of lower molecular weight compounds can be obtained.

[0007] The process of the invention comprises mixing a base starch with acid, drying the mixture to a substantially anhydrous state and heating the dried mixture for a sufficient time to produce a converted starch having a funnel flow viscosity of from about 5 to about 50 seconds.

[0008] The dry converted starches prepared via the foregoing process have a higher level of low molecular weight compounds than corresponding dry converted starches prepared via conventional aqueous acid conversion processes. The converted starches of the present invention demonstrate unique properties and, accordingly are useful in a number of products including adhesives, encapsulation matrices, confectioneries and paper surface sizing products.

[0009] The present invention relates to a process for converting starches with acid to give products having low viscosity and high levels of lower molecular weight compounds.

[0010] All starches and flours (hereinafter "starch") may be suitable for use as the base starch herein and may be derived from any native source. A native starch as used herein, is one as it is found in nature. Also suitable are starches derived from a plant obtained by standard breeding techniques including crossbreeding, translocation, inversion, transformation or any other method of gene or chromosome engineering to include variations thereof. In addition, starches derived from a plant grown from artificial mutations and variations of the above generic composition which may be produced by known standard methods of mutation breeding are also suitable for use as the base starch herein.

[0011] Typical sources for the base starches are cereals, tubers, roots, legumes and fruits. The native source can be corn, pea, potato, sweet potato, banana, barley, wheat, rice, sago, amaranth, tapioca, arrowroot, canna, sorghum, and waxy or high amylose varieties thereof. As used herein, the term "waxy" is intended to include a starch or flour containing at least about 95% by weight amylopectin and the term "high amylose" is intended to include a starch or flour containing at least about 40% by weight amylose.

[0012] Chemically modified starches may also be used as the base starch. Such chemical modifications are intended to include, without limitation, crosslinked starches, acetylated and organically esterified starches, hydroxyethylated and hydroxypropylated starches, phosphorylated and inorganically esterified starches, cationic, anionic, nonionic, and zwitterionic starches, and succinate and substituted succinate derivatives of starch. Procedures for modifying starches are well-known and described, for example in Modified Starches: Properties and Uses, Ed. Wurzburg, CRC Press, Inc., Florida (1986).

[0013] Physically modified starches may also be used as the base starch, including, without limitation, thermally inhibited or pregelatinized starches. Procedures for preparing thermally inhibited starches are disclosed, for example, in U.S. Pat. No. 6,221,420, and references disclosed therein, the disclosure of which is incorporated by reference. Exemplary processes for preparing pregelatinized granular starches are disclosed in U.S. Pat. No. 4,280,851, U.S. Pat. No. 4,465,702, U.S. Pat. No. 5,037,929, and U.S. Pat. No. 5,149,799, the disclosures of which are incorporated by reference.

[0014] Whereas starches acid converted via conventional processes have been produced by dispersing the granular starch in water and adding acid to the mixture, it has now been discovered that mixing a base starch with acid, drying the mixture to a substantially anhydrous state and heating the dried mixture for a sufficient time to produce a converted

starch having a funnel flow viscosity of from about 5 to about 50 seconds produces a starch having unique properties.

[0015] By a substantially anhydrous state means the starch mixture is dried to a moisture content of less than about 1%.

[0016] Generally, a base starch having less than about 18% moisture, is placed into a reactor having a convective and conductive energy source. Such reactors include, without limitation, a fluidized bed, a thin layer thermal reactor or a pressurized mixer equipped with vacuum and a heated jacket. A fluidizing gas (e.g. air) is then introduced at a rate whereby the starch is suspended in the reactor bed. Anhydrous acid (e.g. hydrochloric acid) and a carrier gas (e.g. nitrogen), are injected directly into the fluidizing gas of the fluidized reactor to effect the mixture of the starch and acid.

[0017] The temperature of the bed is increased to a temperature in the range of between about 50 to about 135 °C.

The increase in temperature may be accomplished by means well known in the art including, without limitation, an oil-heated jacket or via a heated air source, or combinations thereof. Depending on the degree of acidification and initial moisture content, the reaction is typically completed within about 3 minutes to about one hour. Where the process is continuous, the process typically takes from about 3 minutes to about 30 minutes. A batch process is typically completed in from about 30 minutes to about one hour. While the reaction is substantially complete in less than about one hour, longer periods of heating, e.g. up to about 6 to about 8 hours or more, may be used without substantial deterioration of the final converted product. After the process is complete, the reactor is cooled and the starch discharged and used without the need for further purification.

[0018] In contrast, a conventional aqueous acid conversion process typically requires from about 12 to about 20 hours, and relatively more acid to effect the conversion of the starch, as well as additional purification and processing in the form of neutralization, filtration and drying. Since the purification process washes out low molecular weight components, the converted starches of the present invention which do not require purification, demonstrate a greater level of low molecular weight components than the corresponding converted starches prepared via a conventional aqueous procedure.

[0019] By adjusting the moisture content, degree of acidity and reaction conditions, the efficient process of the present invention may be tailored to produce a converted starch containing differing levels of lower molecular weight components. Additionally, the anhydrous process of the present invention enables the production of highly converted starches in a highly controlled and reproducible manner having a composition that would not allow for recovery if reacted in the presence of water (i.e., traditional aqueous batch processing). For example, products having a higher degree of conversion, which cannot easily be recovered from water, can be accomplished by preparing the starch according to the process of the present invention.

[0020] The starch compositions produced via this process demonstrate unique performance in certain products. Adhesives and encapsulation matrixes, for example, often require the addition of low molecular weight oligosaccharides or sugars to be added to the formulation for optimum performance. The starch compositions of the present invention advantageously provide desirable products without the need for the addition of lower molecular weight components. Further, the starches of the present invention are useful in products requiring unique gels and textures, including, for example confectioneries and paper surface sizing applications.

[0021] The following methods and examples are presented to further illustrate and explain the present invention and should not be taken as limiting in any regard. All parts and percentages are given by weight and all temperatures in degrees Celsius (°C) unless otherwise noted.

EXAMPLES

[0022] In the examples, the following test procedures were used.

Measurement of Flow Viscosity

[0023] Flow viscosity, also referred to herein as funnel flow viscosity, may be measured as follows. First, the starch must be collected and dried to below 12% moisture in an oven. After the moisture content is determined, tare a stainless steel beaker and thermometer. Add 19% starch to distilled water for a total of 300 g of starch and water. Cook the mixture in a boiling water bath for 15 minutes, stirring for the first 5 minutes. Cover the stainless steel beaker for the remaining 10 minutes. After the cook is complete, remove the beaker from the boiling water bath and cool to 80°F. Bring the beaker back to the original weight before the cook with distilled water and continue cooling to 72°F. Transfer the contents of the beaker to a 100 ml cylinder.

[0024] Flow viscosity, also referred to herein as funnel viscosity, is measured using a fixed orifice viscosity funnel, and is a measurement of the time it takes 100mL of the cook to pass through the orifice. The funnel used to measure flow viscosity is a standard 58 degree, thick-wall, heat resistant glass funnel whose top diameter is about 9 to about 10 cm with the inside diameter of the stem being about 0.381 cm. The glass stem of the funnel is cut to an approximate length of 2.86 cm from the apex, carefully fire-polished, and refitted with a long stainless steel tip which is about 5.08

cm long with an outside diameter of about 0.9525 cm. The interior diameter of the steel tip is about 0.5952 cm at the upper end where is attached to the glass stem and about 0.4445 cm at the outflow end with the restriction in the width occurring at about 2.54 cm from the ends. The steel tip is attached to the glass funnel by means of a Teflon tube. The funnel is calibrated so as to allow 100 mL of water to go through in six seconds using the procedure described below:

[0025] A finger is placed over the orifice of the funnel and the contents are poured from the cylinder into the funnel. A small amount is allowed to flow back into the cylinder to remove trapped air. The balance is poured back into the funnel, and the cylinder is inverted over the funnel, and the contents are allowed to drip from the cylinder into the funnel. The finger is removed from the orifice of the funnel and the length of time is recorded that takes 100 ml of the sample to flow through the apex of the funnel. This time is the flow viscosity of the starch sample.

Measurement of Water Fluidity

[0026] Water fluidity (WF), as used herein, is an empirical test of viscosity measured on a scale of 0-90 wherein fluidity is Inversely proportional of viscosity. Water fluidity of starches is typically measured using a Thomas Rotational Shear-type Viscometer (commercially available from Arthur A. Thomas CO., Philadelphia, PA), standardized at 30°C with a standard oil having a viscosity of 24.73 cps, which oil requires 23.12±0.05 sec for 100 revolutions. Accurate and reproducible measurements of water fluidity are obtained by determining the time which elapses for 100 revolutions at different solids levels depending on the starch's degree of conversion: as conversion increases, the viscosity decreases and the WF values increase.

Measurement of Retained Solids In Converted Starches

[0027] Starch (5 grams) is added to 95 grams of water and stirred for 20 minutes. The slurry is filtered through fluted filter paper. The filtrate is collected on the lens of a calibrated starch refractometer (calibrated to zero using water) where the % solubles is measured.

Measurement of Starch Color (L value)

[0028] A Hunter ColorQUEST spectrophotometer sphere model (commercially available from Hunter Associates Laboratory, Inc., Reston, Va.) equipped with an NIR compression cell with quartz window (commercially available from Bran-Luebbe, Inc., Buffalo Grove, Ill.) is used to measure color according to the manufacture's instructions using the following parameters: Scale=L, Observer angle=10, Illuminant=D65, Reflectance setting=RSIN, Viewing area Size=LAV and Ultraviolet Filter=out.

EXAMPLE 1

Preparation of a Thermally Converted Starch

[0029] Corn starch (4000 grams, obtained from National Starch and Chemical Co.) substituted with 5% propylene oxide was added to a laboratory model fluid bed dryer (6 inch diameter by 15 inch high, Procedyne Corporation, New Brunswick, NJ). The starch was fluidized with air in order to suspend the starch in the bed.

[0030] Anhydrous HCl gas (3.1 grams) is metered into the bed thorough the distributor plate. This produced a starch having a pH of 2.9. The amount of HCl added was determined by measuring the weight loss of the gas cylinder prior to and after the delivery of the gas into the reactor. Nitrogen gas was used to purge all lines prior to and after the addition of the acid in order to ensure that the actual amount of acid was contacted with the starch.

[0031] The temperature of the air flowing into the bed and the temperature of the bed's jacket was then raised to a temperature of 104 °C. After 1 hour the starch was discharged from the bed. The resulting product had a funnel viscosity of 15.2 seconds and a white color similar to the initial starting material.

EXAMPLE 2

Comparison of the Relative Efficiency and Products of Aqueous and Thermal Conversion

[0032] This example illustrates the efficiency of the thermal conversion process as well as the nature of the products compared to the process and products of a conventional aqueous conversion method.

[0033] An acid converted starch was produced according to conventional techniques using an aqueous slurry of starch. Briefly, a stirred 40% solids slurry of native tapioca starch was adjusted to a temperature of 52 °C in a water bath. Concentrated hydrochloric acid was added directly to the slurry and the reaction mixture stirred for 14 hours.

The reaction mixture was adjusted to a pH of 4.5 using sodium carbonate and then to a final pH of 5.5 with dilute sodium hydroxide. The resulting converted starch was washed with water, filtered out of solution and allowed to air dry. Three different trials were conducted on the tapioca starch via this "aqueous" method utilizing different amounts of acid to obtain three converted starches having different water fluidities (Samples A, B, and C).

[0034] For comparison, three samples of the native tapioca starch were converted (Samples D, E and F) according to the method of Example 1 to different water fluidities. This did not require differing amounts of acid.

[0035] Their water fluidities ("WF"), amount of retained solids and color values of Samples A-F were measured according to the Methods described above. The data obtained is recorded in Table 1.

Table 1

Sample #	Method of Conversion	% Acid Used (by weight of dry starch)	WF	Retained Solubles (%)	Color (Hunter "L" value)
A	aqueous	0.7	67	0.52	92.9
B	aqueous	1.15	77	0.79	92.4
C	aqueous	2.00	80	1.57	92.5
D	dry	0.38	78	4.10	93.0
E	dry	0.38	83	30.1	93.7
F	dry	0.38	90	79.8	
D	dry(washed)			0.5	
E	Dry (washed)			4.9	
F	Dry (washed)			16.9	

[0036] As can be seen from the data presented in the Table, the thermally converted starches of the present invention (made according to the "dry" method) achieve higher degrees of conversion, as expressed by relative water fluidities, than the aqueous method of conversion ("aqueous") while using less acid, demonstrating that the dry conversion method is a more efficient process.

[0037] The difference in processes did not negatively impact the color of the converted starches as demonstrated by the comparable color values of the final products. Further, the products of the thermal conversion may be used without washing and, accordingly, advantageously retain a much higher level of low molecular weight solids. Alternatively, the thermally converted starches may be washed to manipulate the degree of solubles content.

[0038] Many modifications and variations of this invention can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. The specific embodiments described herein are offered by way of example only, and the invention is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled.

Claims

1. A process for converting starch comprising mixing a base starch with an acid, drying the mixture to a substantially anhydrous state and heating the dried mixture for a time sufficient to produce a converted starch having a funnel flow viscosity of from about 5 to about 50 seconds.
2. The process of Claim 1 wherein the process is achieved via a fluidized bed conditions.
3. The process of Claim 2 wherein the dried mixture is heated for less than about one hour.
4. The process of Claim 3 wherein the process is conducted as a batch process,
5. The process of Claim 3 wherein the process is conducted as a continuous process.
6. A dry converted starch having a retained solubles content greater than that of the corresponding dry converted starch prepared via conventional aqueous acid conversion methods.

7. A product comprising the starch of Claim 6.
8. The product of Claim 7 wherein the product is selected from the group consisting of adhesives, encapsulation matrices, confectioneries and paper surface sizing applications.
9. A method of using the converted starch of Claim 1 to confer unique gelling and textural properties to products.

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PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 02 01 6934
shall be considered, for the purposes of subsequent
proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 953 579 A (NAT STARCH CHEM INVEST) 3 November 1999 (1999-11-03) * paragraphs [0030]-[0033] *	1-9	C08B30/00 C08B30/12 C08B30/18 C08B31/00 A23L1/0522
X	US 3 967 975 A (IDASZAK LEO R) 6 July 1976 (1976-07-06) * column 4, line 62 - column 5, line 32 *	1-9	
X	US 2 845 368 A (FREDRICKSON RALPH E C) 29 July 1958 (1958-07-29) * column 1, line 47 - column 2, line 8 * * column 3, line 9 - line 73 *	1-9	
X	DATABASE WPI Section Ch, Week 198310 Derwent Publications Ltd., London, GB; Class D17, AN 1983-22726K XP002219692 -& DD 157 347 A (VEB STAERKE GOLSSSEN), 3 November 1982 (1982-11-03) * claim 1 *	1-9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			A23L C08B
INCOMPLETE SEARCH The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims. Claims searched completely : Claims searched incompletely : Claims not searched : Reason for the limitation of the search: see sheet C			
Place of search MUNICH		Date of completion of the search 11 November 2002	Examiner Popa, M
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	

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INCOMPLETE SEARCH
SHEET C

Application Number

EP 02 01 6934

Claim(s) searched completely:
2,3,4,5

Claim(s) searched incompletely:
1,6,7,8,9

Reason for the limitation of the search:

Present claim 1 relates to a process defined (inter alia)
by reference to the following parameter:

P1: funnel flow viscosity of from about 5 to about 50 seconds

The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 84 EPC. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to: "A process for converting starch comprising mixing a base starch with an acid, drying the mixture to a substantially anhydrous state and heating the dried mixture." (see also Guidelines C-III, 4.7a).

The parts relating to the embodiments mentioned in the description at pages 4 and the examples (1, 2) have been subjected to the search procedure and the relevant documents are included in the Search Report.

Present claims 6-8 relate to a product defined by reference to a desirable characteristic or property, namely "having a retained solubles content greater than that of the corresponding dry converted starch prepared via conventional aqueous acid conversion methods".

The claims cover all products having this characteristic or property, whereas the application provides support within the meaning of Article 84 EPC and/or disclosure within the meaning of Article 83 EPC for only a very limited number of such products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 84 EPC). An attempt is made to define the product by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out only for the first part of the claim 6 (and subsequent dependent claims), namely "A dry converted starch" (see also Guidelines C-III, 4.7). Additionally, the presence of such a feature (i.e., the deleted part) will not make the distinction over prior art provided the rest of the features are found simultaneously.

Claim 9 lacks technical features therefore it has been disregarded and its search has been carried out only for the first part, namely: "A method of using the converted starch of claim 1" (see also the remarks on claim 1).



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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	GB 853 828 A (A E STALEY MFG COMPANY) 9 November 1960 (1960-11-09) * page 1, line 20 - line 34 * * page 1, line 74 - line 86 * * page 2, line 38 - line 129 * * claims 1-7 * ---	1-9	
X	EP 0 616 776 A (MATSUTANI KAGAKU KOGYO KK) 28 September 1994 (1994-09-28) * page 2, line 56 - page 3, line 19 * ---	1-9	
X	US 4 510 166 A (LENCHIN JULIANNE M ET AL) 9 April 1985 (1985-04-09) * column 4, line 2 - line 40 * ---	1-9	
X	US 4 280 851 A (PITCHON ESRA ET AL) 28 July 1981 (1981-07-28) * column 2, line 39 - line 44 * * column 2, line 65 - column 3, line 8 * * column 8, line 45 - line 58 * * column 9, line 40 - line 66 * ---	1-9	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	US 5 380 717 A (OHKUMA KAZUHIRO ET AL) 10 January 1995 (1995-01-10) * column 2, line 40 - column 3, line 9 * * examples REF.,1,,REF.,3 * ---	1-9	
X	US 5 410 035 A (WAKABAYASHI SHIGERU ET AL) 25 April 1995 (1995-04-25) * examples REF.,1,,REF.,2 * ---	1-9	
X	EP 0 485 304 A (MATSUTANI KAGAKU KOGYO KK) 13 May 1992 (1992-05-13) * page 3, line 8 - line 13 * ---	1-9	
X	EP 0 368 451 A (MATSUTANI KAGAKU KOGYO KK) 16 May 1990 (1990-05-16) * page 2, line 41 - line 51 * ---	1-9	

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European Patent
Office

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Application Number
EP 02 01 6934

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	ROHWER R.G., KLEM R.E.: "Acid-modified starch: Production and uses", STARCH: CHEMISTRY AND TECHNOLOGY, WHISTLER R.L., NEW YORK, ACADEMIC PRESS, ORLANDO, US, ED. 2, PAGES 529-541 XP002219691 ISBN: 0-12-746270-8 * page 536 *	1-9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)

EPO FORM 1503 03/02 (P/C10)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 01 6934

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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11-11-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0953579 A	03-11-1999	US 6191116 B1	20-02-2001
		EP 0953579 A2	03-11-1999
		JP 2000026502 A	25-01-2000
US 3967975 A	06-07-1976	AR 208418 A1	27-12-1976
		AR 218215 A1	30-05-1980
		AT 369667 B	25-01-1983
		AT 896575 A	15-06-1982
		AT 369288 B	27-12-1982
		AT 896675 A	15-05-1982
		AU 8691975 A	02-06-1977
		AU 8693875 A	02-06-1977
		BE 835887 A1	25-05-1976
		BE 835888 A1	25-05-1976
		BR 7507801 A	10-08-1976
		BR 7507802 A	10-08-1976
		CA 1069277 A1	08-01-1980
		CA 1069275 A1	08-01-1980
		CH 613874 A5	31-10-1979
		CH 620839 A5	31-12-1980
		DE 2552881 A1	02-06-1977
		DE 2552891 A1	26-05-1976
		DK 528275 A ,B	26-05-1976
		DK 528375 A ,B	26-05-1976
		ES 442913 A1	01-04-1977
		ES 443132 A1	16-09-1977
		FI 753304 A ,B,	26-05-1976
		FR 2291787 A1	18-06-1976
		FR 2291788 A1	18-06-1976
		GB 1498206 A	18-01-1978
		GB 1482869 A	17-08-1977
		HU 171560 B	28-02-1978
		HU 173973 B	28-10-1979
		IT 1049867 B	10-02-1981
		IT 1054911 B	30-11-1981
		JP 51076169 A	01-07-1976
		JP 1245138 C	25-12-1984
		JP 51077579 A	05-07-1976
		JP 59003200 B	23-01-1984
		NL 7513763 A ,B,	28-05-1976
		NL 7513765 A	28-05-1976
		SE 408020 B	14-05-1979
		SE 7513172 A	26-05-1976
		SE 416023 B	24-11-1980
		SE 7513173 A	26-05-1976
		US 4021927 A	10-05-1977

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 01 6934

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

11-11-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3967975 A		YU 298775 A1	18-06-1982
		ZA 7507357 A	24-11-1976
US 2845368 A	29-07-1958	NONE	
DD 157347 A	03-11-1982	DD 157347 A1	03-11-1982
GB 853828 A	09-11-1960	BE 569832 A	
		FR 1209303 A	01-03-1960
EP 0616776 A	28-09-1994	JP 3146086 B2	12-03-2001
		JP 6276959 A	04-10-1994
		DE 69419335 D1	12-08-1999
		DE 69419335 T2	23-03-2000
		EP 0616776 A2	28-09-1994
US 4510166 A	09-04-1985	AT 63204 T	15-05-1991
		AU 549987 B2	20-02-1986
		AU 3697284 A	25-07-1985
		CA 1226167 A1	01-09-1987
		DE 3484562 D1	13-06-1991
		DK 25985 A	20-07-1985
		EP 0149258 A2	24-07-1985
		JP 60164449 A	27-08-1985
		JP 6105652 A	19-04-1994
		ZA 8409843 A	28-08-1985
US 4280851 A	28-07-1981	AT 9168 T	15-09-1984
		AU 540982 B2	13-12-1984
		AU 6538580 A	16-07-1981
		CA 1172091 A1	07-08-1984
		CA 1203117 A2	15-04-1986
		DE 3069087 D1	04-10-1984
		EP 0032296 A2	22-07-1981
		IE 50401 B1	16-04-1986
		US 4600472 A	15-07-1986
US 5380717 A	10-01-1995	JP 2007645 C	11-01-1996
		JP 3244365 A	31-10-1991
		JP 7028694 B	05-04-1995
		AT 114934 T	15-12-1994
		DE 69105546 D1	19-01-1995
		DE 69105546 T2	20-04-1995
		DE 443788 T1	30-04-1992
		EP 0443788 A1	28-08-1991
		ES 2044797 T1	16-01-1994

EPO FORM P049

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 01 6934

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

11-11-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5380717 A		KR 181312 B1	01-02-1999
US 5410035 A	25-04-1995	JP 2019839 C	19-02-1996
		JP 4091765 A	25-03-1992
		JP 7045521 B	17-05-1995
		AT 131007 T	15-12-1995
		DE 69115160 D1	18-01-1996
		DE 69115160 T2	09-05-1996
		EP 0470895 A1	12-02-1992
		KR 201350 B1	15-06-1999
EP 0485304 A	13-05-1992	JP 4173094 A	19-06-1992
		DE 485304 T1	18-03-1993
		EP 0485304 A2	13-05-1992
		ES 2044798 T1	16-01-1994
		US 5430141 A	04-07-1995
EP 0368451 A	16-05-1990	JP 1756954 C	23-04-1993
		JP 2100695 A	12-04-1990
		JP 4043624 B	17-07-1992
		JP 2145169 A	04-06-1990
		JP 3047831 B	22-07-1991
		JP 2106965 C	06-11-1996
		JP 2154664 A	14-06-1990
		JP 3047832 B	22-07-1991
		DE 68914401 D1	11-05-1994
		DE 68914401 T2	25-08-1994
		EP 0368451 A2	16-05-1990
		KR 135075 B1	20-04-1998
		US 5620873 A	15-04-1997

EPO FORM PUA/EN

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82